

Investigation of Arsenic Oxidation State Speciation in Primary Calibration Solutions and Effects on ICP-OES Measurements

It is well known that the toxicity of arsenic is strongly tied to oxidation state speciation. Less understood is the effect that arsenic oxidation state has on measurement accuracy of analytical instruments used for arsenic determinations. Standards prepared from arsenic metal, which in principle should yield a more accurate and precise instrument calibration relative to those prepared from arsenic salts, were frequently found to have inexplicable disagreements between batches when analyzed using optical emission or mass spectrometry. The deviation, which can at times be as great as 8 %, frustrates the effort of producing accurate clinical measurement of arsenic. We have investigated the apparent deviation, and have traced the problem to differences in arsenic speciation of standards coupled with a systematic error in inductively coupled plasma optical emission spectrometry (ICP-OES) measurements of different arsenic species.

L.L. Yu, T.A. Butler, and G.C. Turk (Div. 839)

The research conducted by the NIST team has revealed that ICP-OES response to arsenic is dependent upon the speciation of the element.

The NIST team designed and conducted experiments that definitively proved that arsenic in the +3 oxidation states yields less atomic emission from an ICP than the same concentration of arsenic in the +5 state.

Because of the difference in response vs oxidation state, there is a significant measurement bias if the chemical form of arsenic differs between samples and standards. The results of a study of the digestion kinetics of arsenic metal used to prepare calibration standards revealed that standards produced from the same source of arsenic metal can yield solutions with different oxidation states.

The study enabled us to develop a procedure for the production of single-species arsenic standards of known oxidation state, which eliminates a source of measurement bias.

Impact: This work should lead to an improvement in the accuracy of all arsenic measurements being performed using ICP-OES or inductively coupled plasma mass spectrometry (ICP-MS).

Future Plans: Other elements with similar chemistry to that of arsenic are likely to exhibit similar behavior. These will be investigated. In addition, the mechanism that causes oxidation state to affect atomic emission intensity from an ICP is not understood. Study of this mechanism could result in improved accuracy of ICP instrumentation.

Reference:

L.L. Yu, T.A. Butler, and G.C. Turk, "Effect of Valence State on ICP-OES Value Assignment of SRM 3103a Arsenic Spectrometric Solution", Anal. Chem. 2006, 78, 1656.